3rd Summer School on nuclear and industrial glasses for energy transition

Modeling Approaches

Atomistic simulation of glass alteration using the Monte Carlo method

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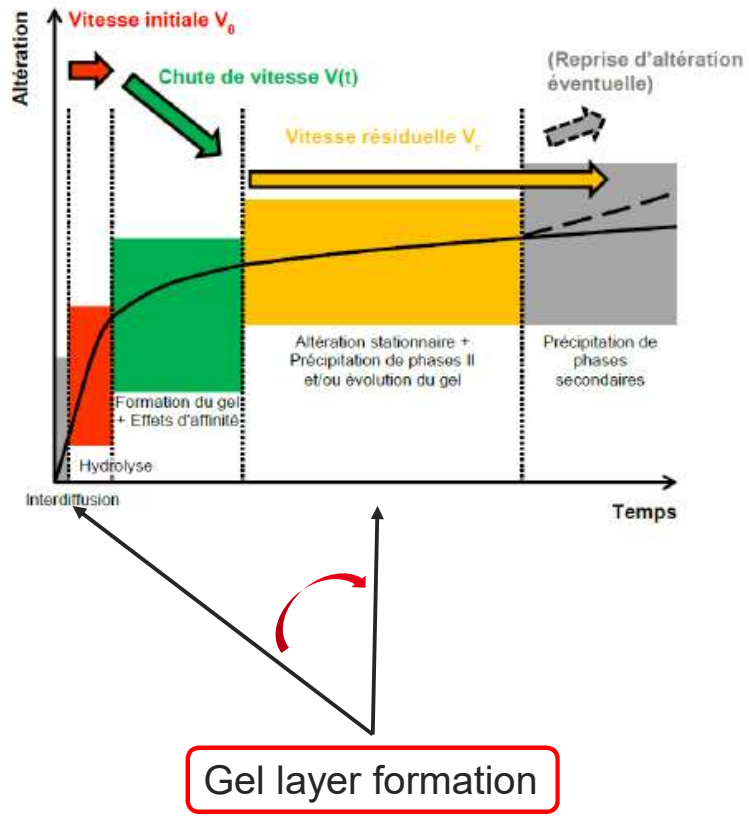
Outline

- Why a Monte Carlo approach to study glass alteration?
- The successive Monte Carlo approaches (1995 – 2020)
- Why is a refined Monte Carlo method needed today?
- Presentation of the refined Monte Carlo method developed at CEA
- Comparison with the experiments
- Conclusions - Perspectives

Why a Monte Carlo approach to study glass alteration



- Understanding the origin of the residual alteration rate is fundamental
- The gel layer formation is in direct relation with the residual alteration rate
- ***Monte Carlo is a tool to simulate the gel layer formation*** *and its impact on the alteration behavior at the atomistic level*

The first Monte Carlo approach

- First work (M. Aertsens, Mol (Belgium), 1995 - 2000)

Application to a SiO_2-Na_2O glass

MODELLING OF GLASS DISSOLUTION WITH A MONTE CARLO METHOD

Marc AERTSENS
SCK•CEN, Boeretang 200,B-2400 Mol, Belgium

Proceedings of the summer school Mejannes le Clap, CEA Valrho (1997)

- Main characteristics of M. Aertsens's method

  - Diamond network with a sparingly soluble element (Si) and a soluble element (Na)
  - Si and Na are randomly distributed on the sites
  - A solution is in contact with the solid
  - A probability is applied to break the Si-Si bonds (P^+) and another is applied to reform a Si-Si bond (P^-, redeposition)

$$\equiv Si - O - Si \equiv + H_2O \rightarrow \equiv Si - OH + \equiv Si - OH$$

  - Released Si can freely diffuse within the solution, following a probability of diffusion P_{diff} (>> P^+ and P^-)

  - Na ions can exchange with water molecules, following the probability P_{ex}.

$$\equiv Si - O - Na + H^+ \rightarrow \equiv Si - O - H + Na^+$$

Relation to the transition state theory

Chemical Reaction $A + B \rightarrow C^* \rightarrow D$

Forward reaction rate $R^+ \propto a_A a_B P^+$ $P^+ = \exp(-\frac{\Delta G_{AB \rightarrow C^*}}{R\,T})$

Backward reaction rate $R^- \propto a_D P^-$ $P^- = \exp(-\frac{\Delta G_{D \rightarrow C^*}}{R\,T})$

Equilibrium constant K $P^- = \frac{P^+}{K}$ $K = \exp(-\frac{\Delta G_{D \rightarrow AB}}{R\,T})$

$$\Delta G_{D \rightarrow AB} = \Delta G_{AB \rightarrow C^*} - \Delta G_{D \rightarrow C^*}$$

Estimation of the model parameters

Only a rough estimation is possible

- P^+ is fitted on the initial dissolution rate of pure silica ($1 g/m^2/j$)
- P^+ and P^- are related to the silica solubility in pure water (10^{-3} mole/l)
- P_{diff} is fitted to reproduce Si diffusion in water ($D_{Si} = 0.7\ 10^{-7}\ m^2/s$)
- The exchange probability is estimated considering data in borosilicate glasses :
  - reaction rate for the exchange = $1.74\ 10^{-11}$ mol/m²/s
  - dissolution rate = $3.03\ 10^{-14}$ mol/m²/s

$$\rightarrow \quad \frac{P_{ex}}{P^+} = 1000$$

- Na and Si diffusion coefficient in water are taken equal

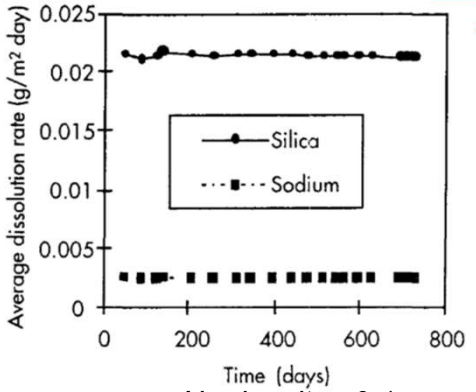
Main results with the first Monte Carlo approach

- The system contains 1200 sites

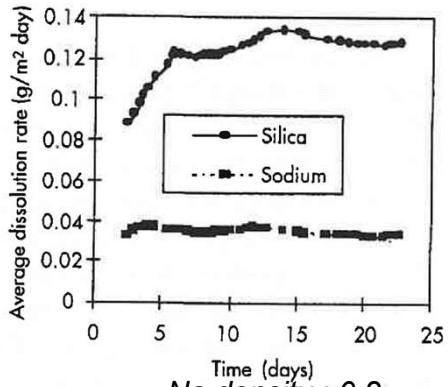
  - The Si and Na dissolution are congruent for the lowest Na content and a protective gel layer is formed at the solid – solution interface

  - Dissolution becomes incongruent at higher Na content due to the formation of a percolating Na network. In this case, the Si ions dissolve in clusters.

Sodium density ρ	Time (days)	Average dissolution rate		Ratio of normalised dissolution rates	Position of surface layer		
		Silica (g/m^2 days)	Sodium (g/m^2 days)		Water side	Glass side	Width
0.1	730.7	0.021	0.0024	1.01	1 074	1 089	15
0.2	22.7	0.13	0.034	1.05	204	255	51
0.3	1	0.38	0.54	3.3	6	147	141
0.4	0.2	0.99	9.5	14.3	0	351	351
0.5	0.04	7.6	69	9.1	0	429	429



Na density : 0.1



Na density : 0.2

The Monte Carlo approach developed at CEA

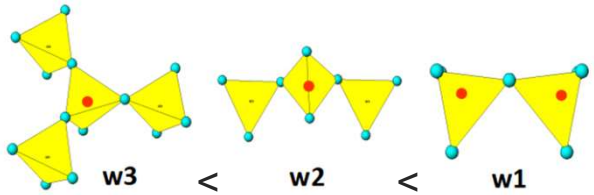
- Development in 2000 – 2010

  - M. Aertsens's method has been modified:

    - ✓ Possibility to consider SiO_2-B_2O_3-Na_2O-CaO-ZrO_2 systems

    - ✓ The diffusion in solution is suppressed to limit the computational time
      → systems containing up to 10^6 atoms can be simulated

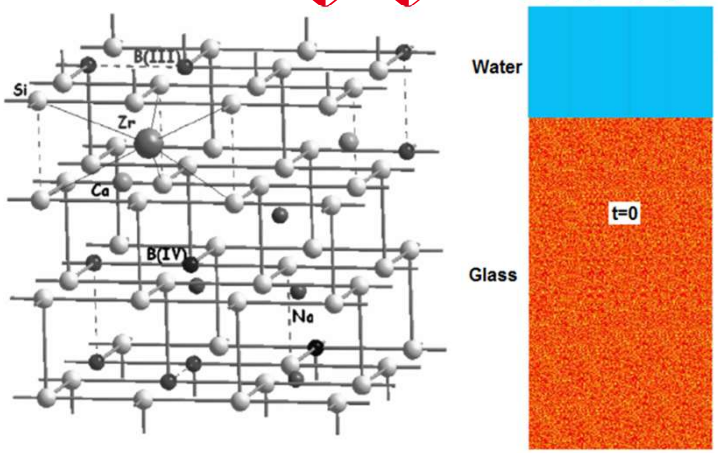
    - ✓ The glass dissolves atom by atom, rather than bond by bond, with probabilities that depend on the local reticulation level



A. Ledieu, PhD, Ecole Polytechnique, 2004
C. Cailleteau et al., Nat. Mater., 7 (2008) 978
M. Arab et al., J. Non-Cryst. Solids, 354 (2008) 155
C. Cailleteau et al., J. Phys. Chem. C, 115 (2011) 5846

The Monte Carlo approach developed at CEA

- A cubic network with removed edges (to have only four coordinated vertices) is used to represent the glass
- B^{III} and B^{IV} are introduced (but suppressing additional edges)
- NBO around the Si ions are introduced (depending on the glass composition)
- Zr is not soluble
- Periodic boundary conditions along two directions parallel to the glass – water interface



Three dissolution probabilities (w_3, w_2 et w_1) to model Si dissolution based on the number of neighbouring Bridging Oxygen (3, 2 or 1)

The redeposition of Si ions can occur based on the probability: $w_c * C_{Si}$

Quantity of Si in solution

$$\frac{dN_{Si}}{dt} \equiv V\frac{dc_{Si}}{dt} = \sum_{i \in S(t)} (w_d(i) - w_c \times c_{Si})$$

Si solubility

$$c^*_{Si} = \frac{\langle w_d(i) \rangle_{i \in S(t)}}{w_c}$$

Two main steps

Dissolution at the glass surface

Redeposition at the glass surface

Formation of the gel layer

Everything occurs on the surface

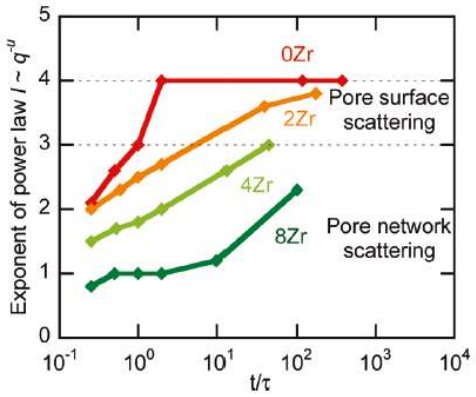
Exploring the Role of Zirconium: An Exemplary Application

- Experiments on 5 oxide glasses: $(61-x)SiO_2–17B_2O_3–18Na_2O–4CaO–xZrO_2$ $(x = 0, 1, 2, 4, 8)$

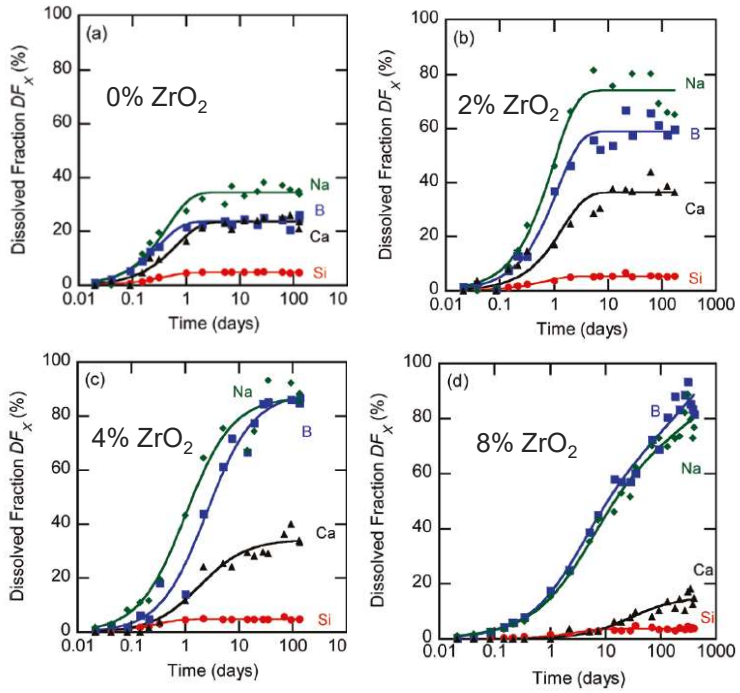
- The forward alteration rate decreases when the $\%ZrO_2$ increases

	r_0 (g/m²/j) pH=6.9 / 8.0
0% ZrO_2	26 / 18.7
2% ZrO_2	4.4 / -
4% ZrO_2	1.1 / 10.9
8% ZrO_2	0.09 / 1.8

- The gel restructuration was measured by SAXS ($I(q)=q^{-u}$). The maturation rate decreases when the $\%ZrO_2$ increases



- But … the durability decreases when the $\%ZrO_2$ increases

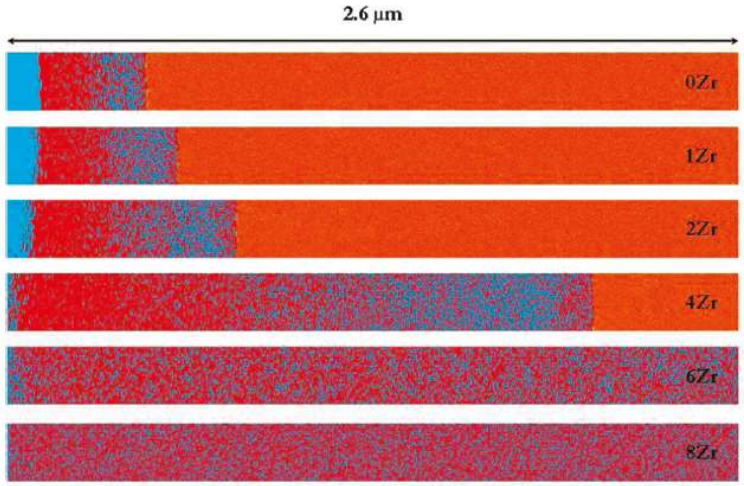


Exploring the Role of Zirconium: An Exemplary Application

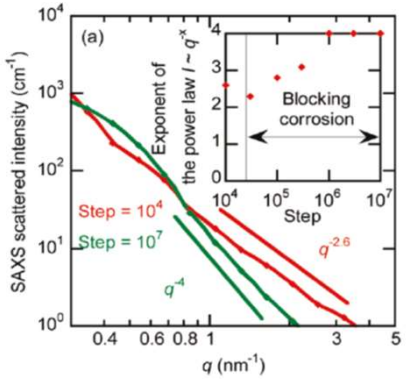
- Monte Carlo simulations using the glass compositions:

$$(61 - x)SiO_2–17B_2O_3–18Na_2O–4CaO–xZrO_2$$
$$(x = 0, 1, 2, 4, 8)$$

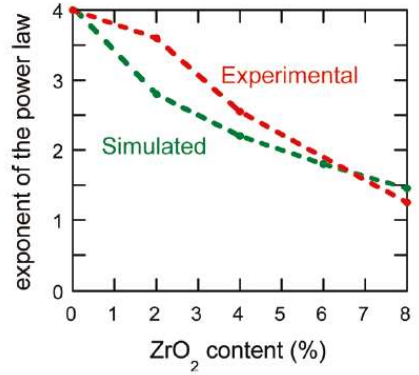
  - The alteration stops for 0%, 2% and 4% ZrO_2
  - The alteration is complete for 6% and 8% ZrO_2.



  - The SAXS spectra were calculated: the gel restructuration is slower when the ZrO_2% increases



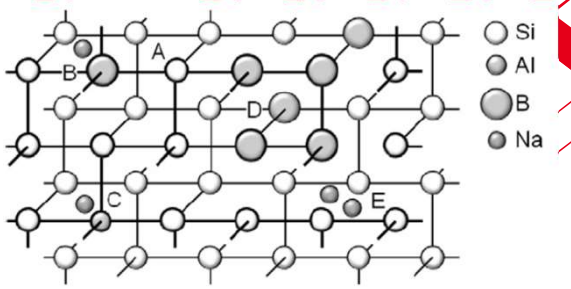
0%ZrO_2



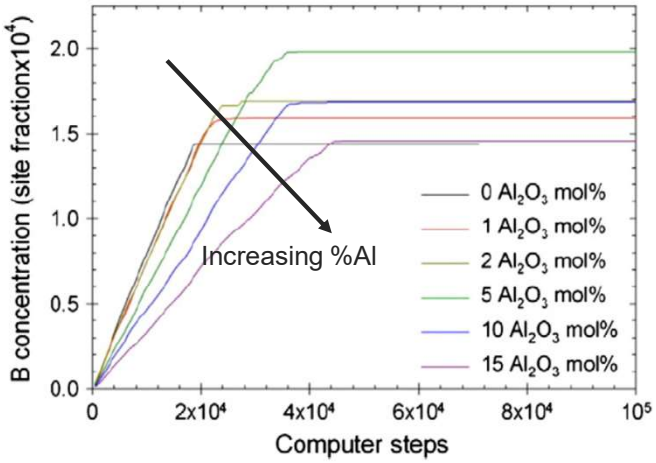
$$F_{S,W}(\tilde{q}) = \frac{1}{n_S}\sum_{n=1}^{n_S}\frac{1}{N_S}\left\{\left[\sum_{i=S\text{ or }W}\cos(\tilde{\mathbf{q}}.\mathbf{r}_i)\right]^2 + \left[\sum_{i=S\text{ or }W}\sin(\tilde{\mathbf{q}}.\mathbf{r}_i)\right]^2\right\}$$

The PNNL Monte Carlo approach

S. Kerisit et al., Geochim. et Cosmochim. Acta, 75 (2011) 5296
S. Kerisit et al., J. Non-Cryst. Solids, 378 (2013) 273
S. Kerisit et al., J. Non-Cryst. Solids, 408 (2015) 142



- The glass composition has been completed
  - Introduction of Al (^{IV}Al) – same qualitative behaviour as Si
  - Boroxol rings can be considered
  - No gel maturation
  - Possibility to take into account precipitation of secondary phases
- Focus on a specific result: Non linear effect of Al
  - The B dissolution rate decreases when $\%Al_2O_3$ increases
  - The altered glass quantity is maximum for intermediate Al_2O_3 content



$(70 - 2x)\%\ SiO_2\ x\%\ Al_2O_3\ 15\%\ B_2O_3\ (15 + x)\%\ Na_2O$

$0 \leq x \leq 15\%$

1) Al hardening effect : the initial B alteration rate decreases

2) %Al↑ : release is slower : the formation of the gel is slower : the plateau is higher

3) %Al↑ : the protective layer is formed closer to the surface : the height of the plateau decreases

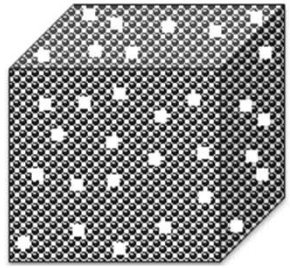
Why is a refined Monte Carlo method needed today?

(collaboration with PNNL – S. Kerisit)

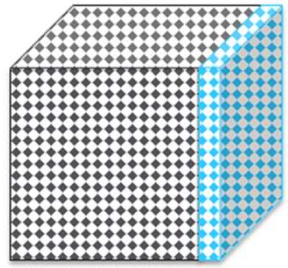
- Glass $65SiO_2–17.5B_2O_3–4.0Al_2O_3–13.5Na_2O$

Radiation effects were simulated by classical MD and implemented in the Monte Carlo simulations

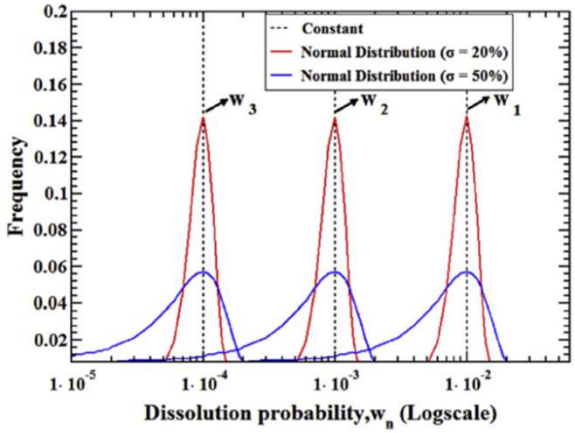
Classical MD	Monte Carlo
Depolymerization	Increase of NBO, $^{[3]}B$ on the network
Increase of disorder	Introduction of distributions for the probabilities



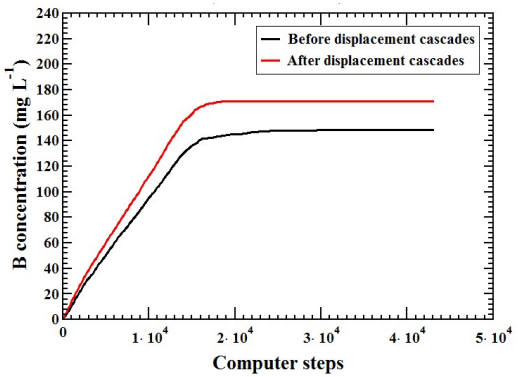
Irradiated Glass



Aqueous Glass dissolution



Swelling and acceleration of water diffusion is not considered



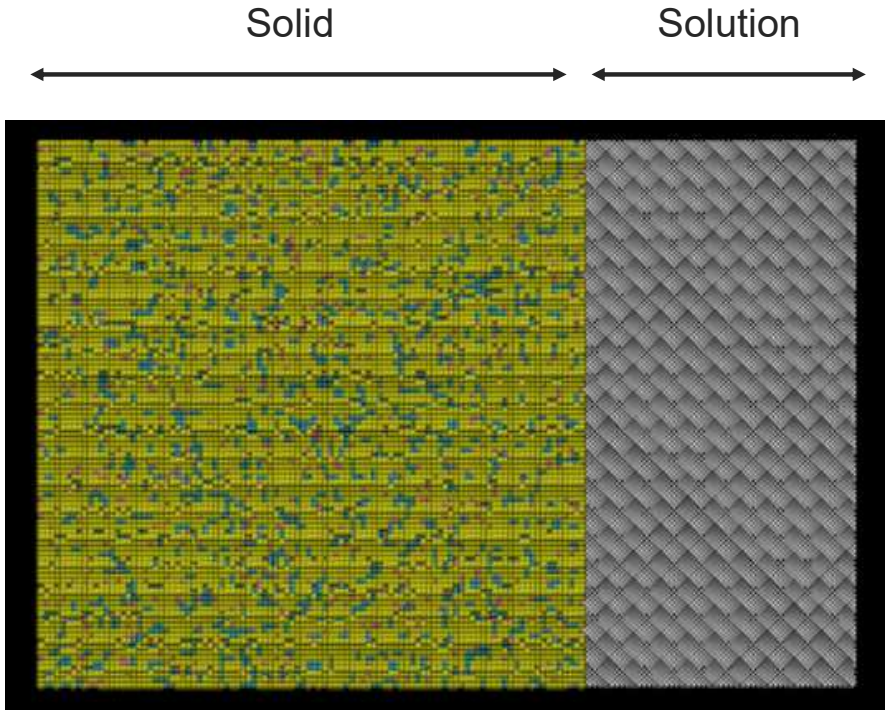
A 15% increase of the alteration depth is observed (X2 or X3 experimentally)

It has not been possible to reproduce the radiation effects without considering diffusion of water in the glass

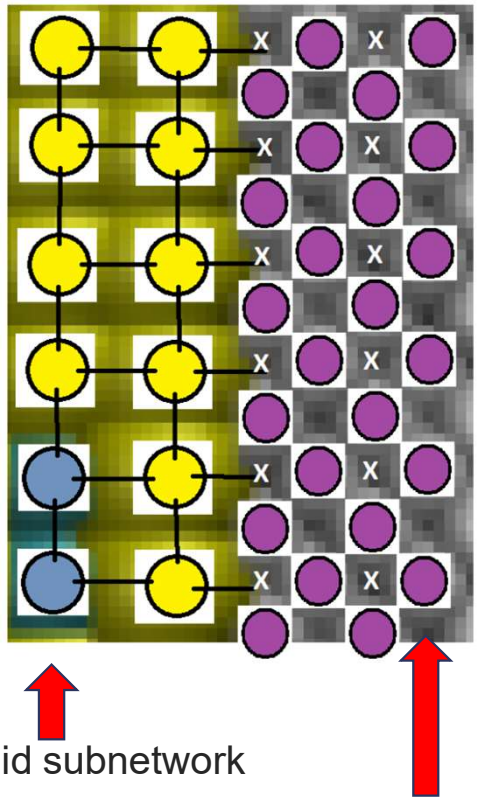
A. Jan et al., J. Non-Cryst. Solids, 519 (2019) 6

A refined version of the Monte Carlo method is under development

- Initial structure: two subnetworks (solid and liquid) interpenetrate



2D images



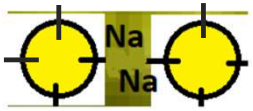
- Solid subnetwork
- Liquid subnetwork (H_2O=W)

Method currently developed for SiO_2-Al_2O_3-B_2O_3-Na_2O glasses

The refined Monte Carlo method

➢ In the initial structure, we have:

Closed bonds 

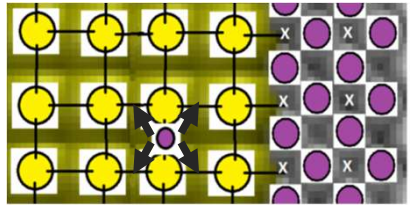
Open bonds 

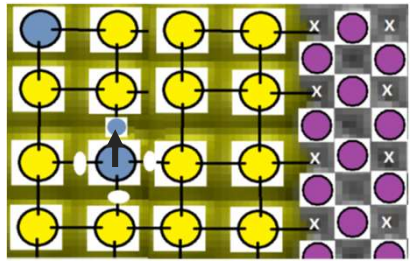
to introduce NBO

Non-existent bonds 
to introduce B^{III}
in addition to B^{IV}

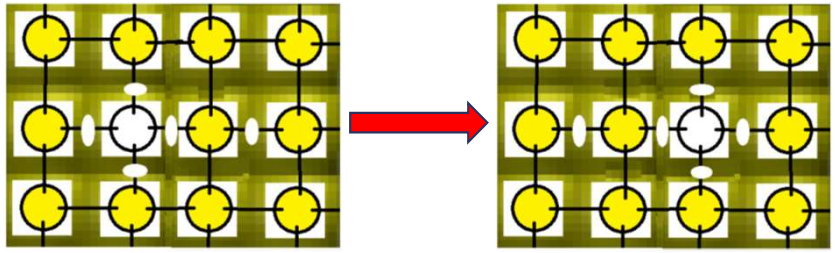
NBO and B^{III} are introduced by pairs as in the previous method

➢ New implemented mechanisms

❖ Water diffusion in the solid 

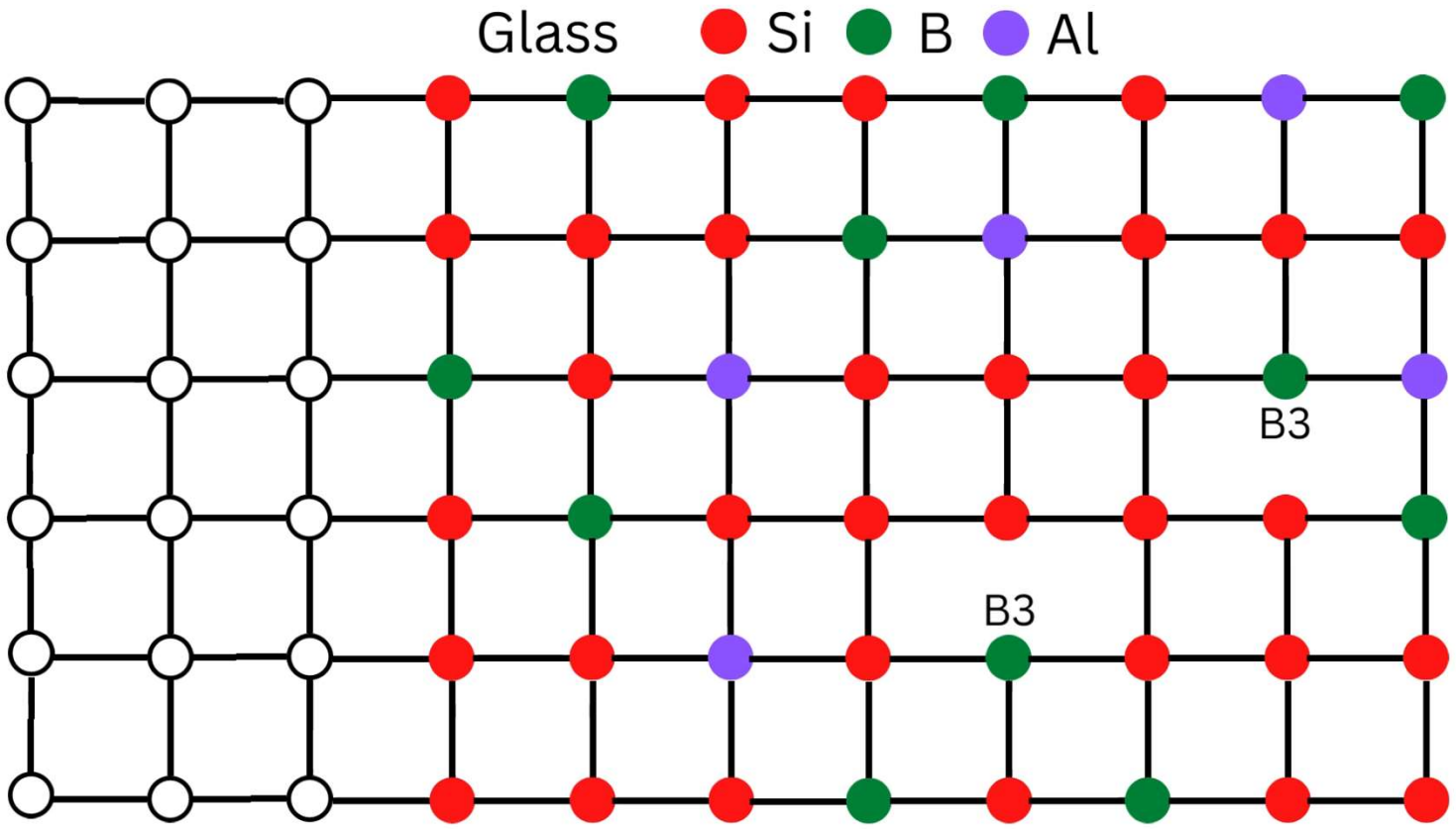
❖ Hydrolysis bond by bond 

❖ Reformation of bonds

❖ Maturation of the gel → vacancy jumps in the solid 

❖ Redeposition of Si and Al at the glass–water interface

The refined Monte Carlo approach



Animation prepared by K. Damodaran

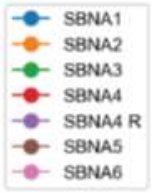
Comparison between Monte Carlo calculations and experiments

Series of 6 glasses: $SiO_2 - Al_2O_3 - B_2O_3 - Na_2O$

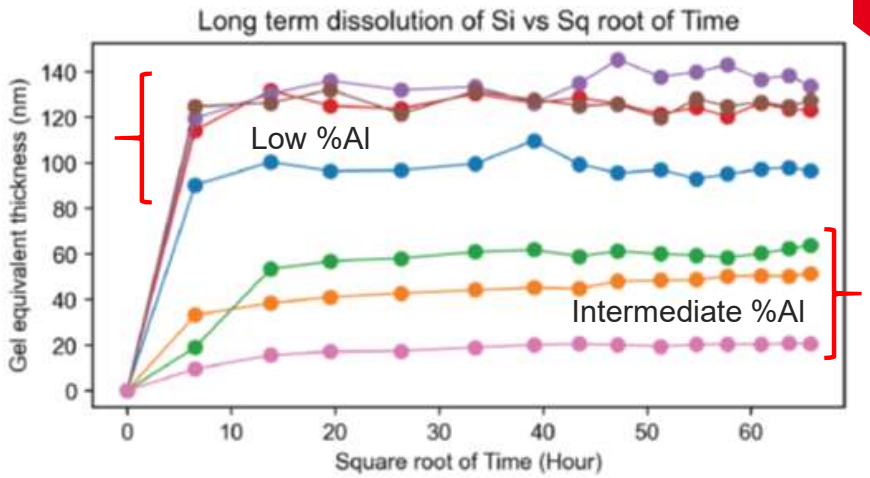
Alteration: 90°C, pH=9, DIW, 180 days, S/V=50cm^{-1}

Molar percentage

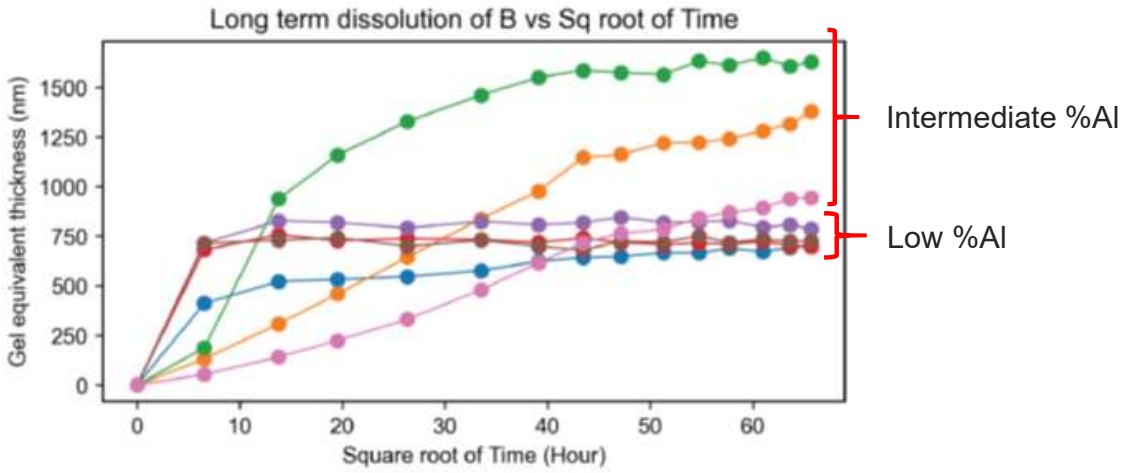
	SiO2	B2O3	Na2O	Al2O3
SBNA1	67,8	18	14,2	0
SBNA2	64,9	17,3	13,7	4,1
SBNA3	60,5	20,1	15,9	3,5
SBNA4	63	18,7	17,3	1
SBNA5	60,5	20,1	18,4	1
SBNA6	66,8	15,9	11,3	6



Si release



B release



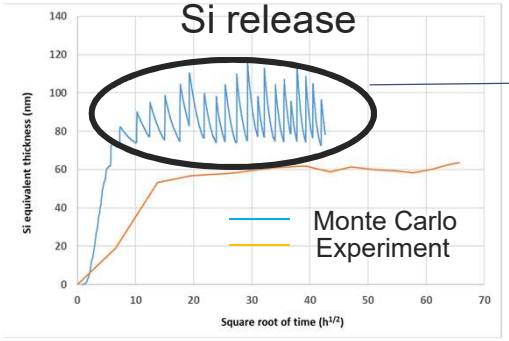
Two different behaviors

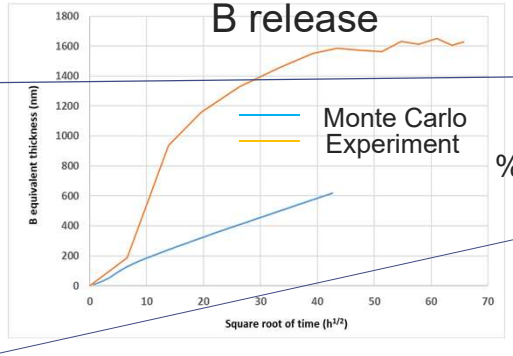
Low $\%Al_2O_3$
→ Large forward alteration rate
→ B release stops rapidly

Intermediate $\%Al_2O_3$
→ Smaller forward alteration rate
→ No halt of the B release

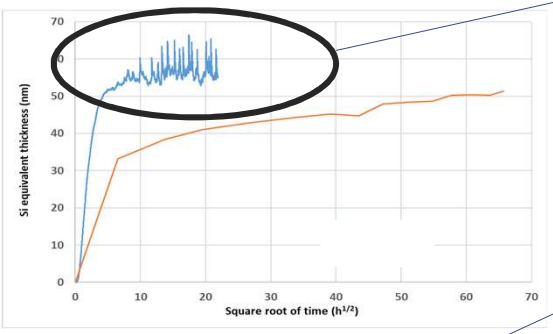
K. Damodaran, PhD thesis, University of Montpellier, 2022

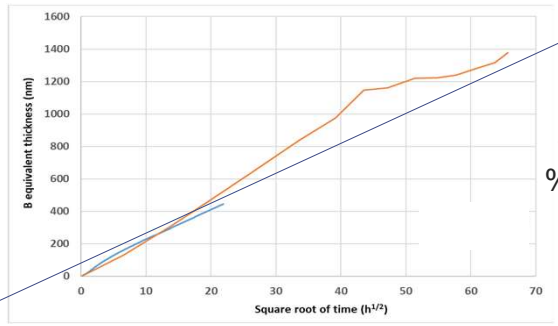
Monte Carlo results



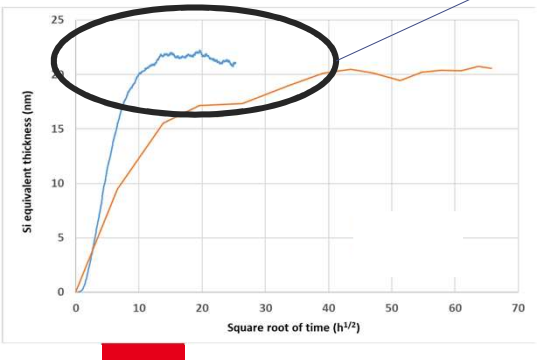


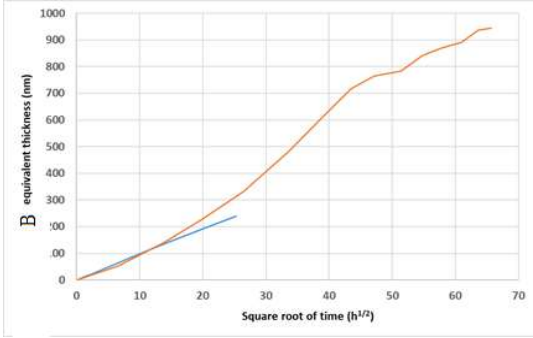
SBNA3
%Al 3.5%





SBNA2
%Al 4.1%





SBNA6
%Al 6%

	SiO_2(mol %)	B_2O_3(mol %)	Na_2O(mol %)	Al_2O_3(mol %)
SBNA3	60.5	20.1	15.9	3.5
SBNA2	64.9	17.3	13.7	4.1
SBNA6	66.8	15.9	11.3	6

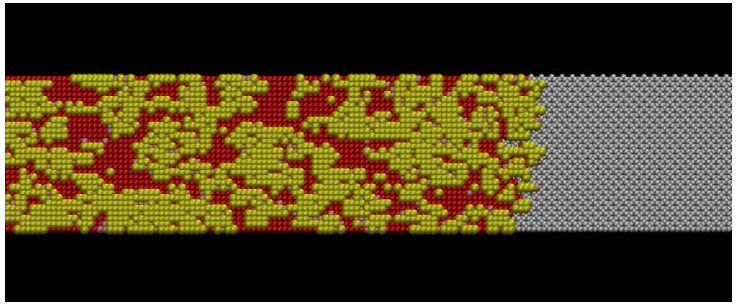
Larger the %B_2O_3 in glass, larger the cluster release

- **The MC parameters were fitted:**
  - **to reproduce the asymptotic value for the Si equivalent thickness**
  - **to reproduce the slope of B equivalent thickness vs. time**

- **The duration of the MC step is calculated by equalizing the experimental and simulation times necessary to reach saturation**

	Experimental time	Monte-Carlo steps	Duration of one step
SBNA3	191.12h	42000 steps	16.38s
SBNA2	43.07h	180000 steps	0.8614s
SBNA6	191.83h	120000 steps	5.75s

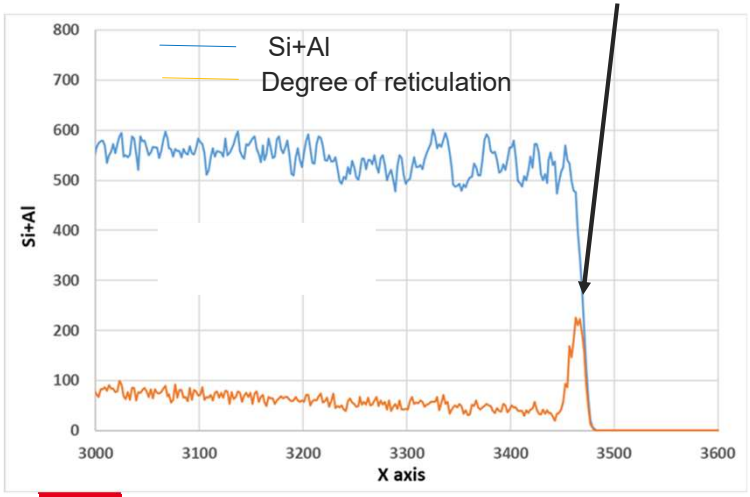
What happens near the glass-water interface ?



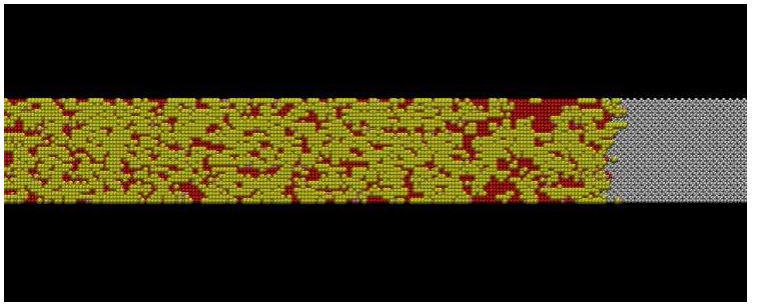
SBNA3 $\%B_2O_3$ 20.1%

400000 steps

An external reticulated zone is formed



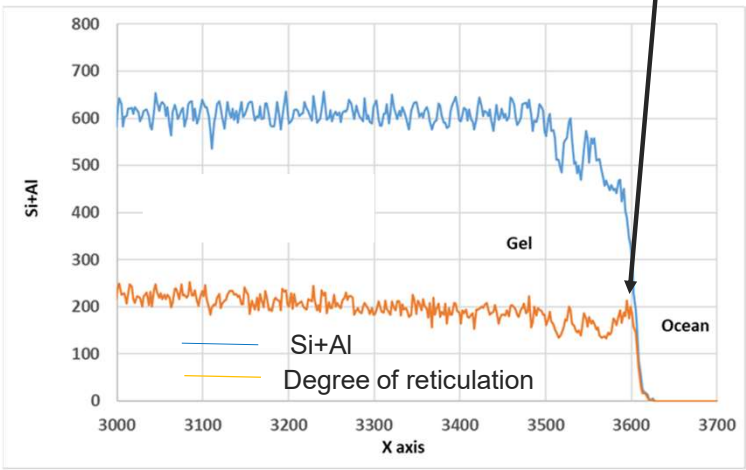
The intensity depends on $\%B_2O_3$



SBNA2 $\%B_2O_3$ 17.3%

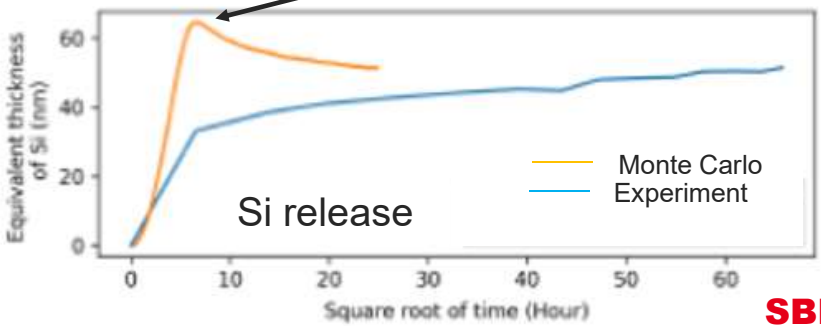
2 X 10^6 steps

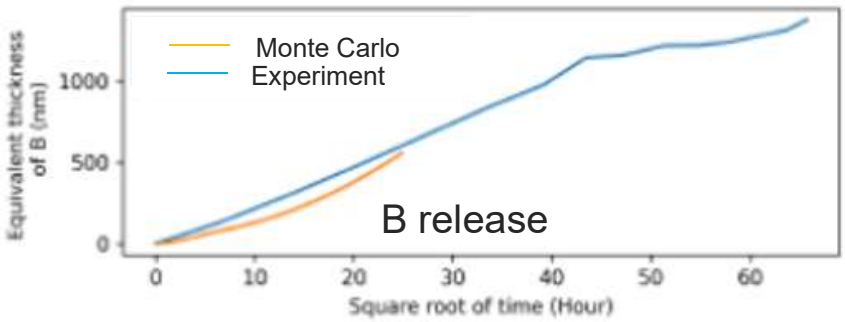
A smaller reticulated zone is formed



Comparison to another Monte Carlo calculation

A peak is observed in the release of Si

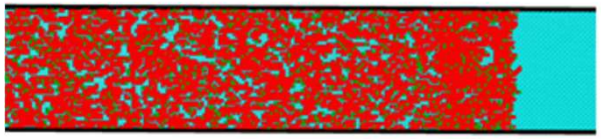


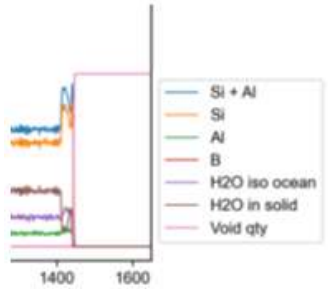


SBNA2

The diffusion of water is modified by promoting jumps inward into the glass

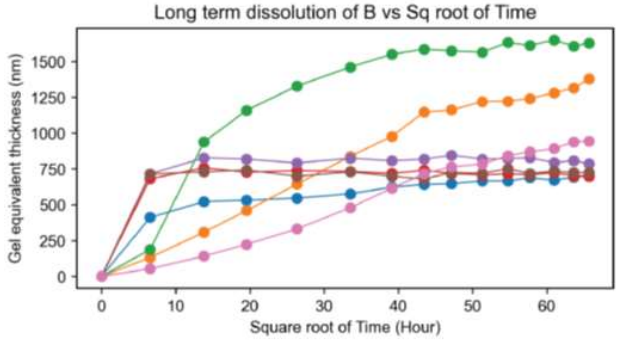
An external layer enriched with Si is observed at the glass-water interface





<u>The following interpretation can be suggested</u>

First case: No peak in the release of Si
→ an external reticulated zone is formed
→ glasses with intermediate %Al?



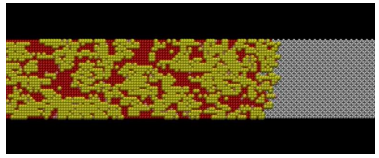
Second case: A peak in the release of Si is observed
→ an external zone enriched with Si is formed
→ glasses with a low %Al?

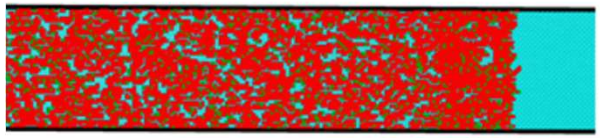
Perspectives

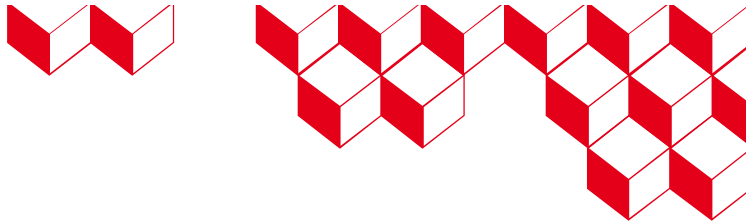
- Parallelization of the Monte Carlo code (we are currently limited by the computational time)
- Investigate the mechanisms behind the formation of the reticulated zone (connexion to the release of clusters?), and the zone enriched with Si
- Study of the gel maturation

Summary

- The Monte Carlo approach: a thirty-year history
- A refined Monte Carlo method is currently under development
- First result: the Si release rate is an important factor that impacts the alteration layer morphology







Thank You for

Your attention